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(54) METHOD FOR PRODUCING HIGH-STRENGTH COPPER BASE ALLOY
WITH HIGH ELECTRICAL CONDUCTIVITY

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Specification

1. Title of the Invention

METHOD FOR PRODUCING HIGH-STRENGTH COPPER BASE ALLOY WITH HIGH ELECTRICAL CONDUCTIVITY

2. Scope of Patent Claim

(1) A method for producing a high-strength copper base alloy with high electrical conductivity, whereby, after solution-annealing a copper base alloy containing 0.1 – 5.0 wt% Ti and 0.1 – 5.0 wt% Sn, with the remainder consisting of Cu and unavoidable impurities, aging is performed for 10 seconds -10 hours at a material temperature of 200 – 700°C, then cold rolling by 10% or more is performed, and further heat treatment for 10 seconds - 10 hours is performed at a material temperature of 200 – 700°C to improve mechanical strength and electrical conductivity.

(2) A method for producing a high-strength copper base alloy with high electrical conductivity whereby after solution-annealing a copper base alloy containing 0.1 – 5.0 wt% Ti and 0.1 – 5.0 wt% Sn and further containing a total of 0.005 – 2.0 wt% of one or two or more of the following: 0.005-1.0 wt.% P, 0.005-1.0 wt.% Al, 0.005-1.0 wt.% Zn, 0.005-1.0 wt.% Ni, 0.005-1.0 wt.% Si, 0.005-0.5 wt.%Pb, 0.005-1.0 wt.% Be, 0.005-1.0 wt.% Fe, 0.005-1.0 wt.% Mn, 0.005-1.0 wt.% Mg, 0.005-1.0 wt.% Cr, 0.005-1.0 wt.% Co, 0.005-1.0 wt.% Zr, 0.005-1.0 wt.% As, 0.005-1.0 wt.% Ag, 0.005-1.0 wt.% Cd, 0.005-1.0 wt.% In, 0.005-1.0

wt.% Sb, 0.005-1.0 wt.% Te, 0.005-1.0 wt.% Ge and 0.005-1.0 wt.% Hf, with the remainder consisting of Cu and unavoidable impurities, aging is performed for 10 seconds -10 hours at a material temperature of 200 – 700°C, then cold rolling by 10% or more is performed, and further heat treatment for 10 seconds - 10 hours is performed at a material temperature of 200 – 700°C to improve mechanical strength and electrical conductivity.

3. Detailed Description of the Invention

[Object]

The present invention pertains to a method of producing high-strength copper base alloys high electrical conductivity having excellent mechanical strength and good conductivity.

[Prior Art and Problems]

Beryllium copper alloys and titanium copper alloys are high-strength copper alloys being used today as high-precision spring materials. Although beryllium copper alloys have a high tensile strength of 90 – 140 kg/mm² and a good conductivity of 20 – 25% IACS, they are extremely expensive because they contain approximately 2% beryllium. Moreover, they have disadvantages in that beryllium is a poisonous substance and beryllium copper alloys become brittle at temperature of 250°C or higher, leading to degradation of the alloy. Moreover, titanium copper alloys have advantages in that they rival beryllium copper alloys in terms of spring performance, heat resistance, and abrasion resistance, and they have approximately the same mechanical strength and are inexpensive, but

they have a major disadvantage in that their electrical conductivity is extremely poor.

Because of this, addition of Sn as a third element to titanium copper alloys has been suggested in order to obtain good conductivity while retaining the mechanical strength of titanium copper alloys. Nevertheless, even if aging treatment, or cold drawing and aging treatment, are performed after conventional solution annealing of tin-containing titanium copper alloys, the tensile strength remains at 80 – 95 kg/mm² at the highest and it is necessary to further improve mechanical strength in order to obtain a substitute alloy for beryllium copper alloys.

[Structure of the Invention]

The present invention is in light of these points, presenting a method of producing high-strength copper base alloys with high electrical conductivity having ideal properties as materials for high-precision springs, by means of which the mechanical strength is further improved while retaining the good electrical conductivity of tin-containing titanium copper alloys and the economic problems as well as problems in terms of toxicity of beryllium copper alloys are avoided.

The present invention relates to a method for producing high-strength copper base alloys with high electrical conductivity, whereby after solution-annealing a copper base alloy containing 0.1 – 5.0 wt% Ti and 0.1 – 5.0 wt% Sn, with the remainder consisting of Cu and unavoidable impurities, or a copper base alloy containing 0.1 – 5.0 wt% Ti and 0.1 – 5.0 wt% Sn and further containing a

total of 0.005 – 2.0 wt% of one or two or more of the following: 0.005-1.0 wt.% P, 0.005-1.0 wt.% Al, 0.005-1.0 wt.% Zn, 0.005-1.0 wt.% Ni, 0.005-1.0 wt.% Si, 0.005-0.5 wt.% Pb, 0.005-1.0 wt.% Be, 0.005-1.0 wt.% Fe, 0.005-1.0 wt.% Mn, 0.005-1.0 wt.% Mg, 0.005-1.0 wt.% Cr, 0.005-1.0 wt.% Co, 0.005-1.0 wt.% Zr, 0.005-1.0 wt.% As, 0.005-1.0 wt.% Ag, 0.005-1.0 wt.% Cd, 0.005-1.0 wt.% In, 0.005-1.0 wt.% Sb, 0.005-1.0 wt.% Te, 0.005-1.0 wt.% Ge and 0.005-1.0 wt.% Hf, with the remainder consisting of Cu and unavoidable impurities, aging is performed for 10 seconds -10 hours at a material temperature of 200 – 700°C, then cold rolling by 10% or more is performed, and further heat treatment for 10 seconds - 10 hours is performed at a material temperature of 200 – 700°C to improve mechanical strength and electrical conductivity.

[Results]

Thus, when [alloys are] produced by the method of the present invention, it is possible to simultaneously and markedly improve the tensile strength and the electrical conductivity.

[Specific Description of the Invention]

The reasons for restricting the alloy components and the production method of the present invention are described next:

The reason for setting the Ti content at 0.1 – 5.0 wt% is that if it is less than 0.1 wt%, the strength that is expected will not be obtained, while exceeding 5.0 wt% is undesirable in terms of improving the electrical conductivity.

The reason for setting the Sn content at 0.1 – 5.0 wt% is that if it is less than 0.1 wt%, the electrical conductivity that is expected will not be obtained,

while if it exceeds 5.0 wt%, the excess Sn, which will not form a solid solution even if heat treatment is performed, will produce an intermetallic compound with the Ti and precipitate as coarse crystals and there will be a marked drop in alloy strength.

The reason for setting the total amount of one or two or more selected from the group consisting of the above-mentioned predetermined amounts of P, Al, Zn, Ni, Si, Pb, Be, Fe, Mn, Mg, Cr, Co, Zr, As, Ag, Cd, In, Sb, Te, Ge, and Hf as auxiliary components at 0.005 – 2.0 wt% is that if it is less than 0.005 wt%, the high strength that is expected as a result of adding auxiliary components will not be obtained, while if it exceeds 2.0 wt%, there will be a marked drop in electrical conductivity and furthermore, solderability and heat workability will deteriorate.

Materials that have been solution-annealed are aged for 10 seconds – 10 hours at a material temperature of 200 – 700°C and cold rolling to a draft of 10% or more is then performed. The reason for performing aging treatment at 200 – 700°C is that the strength and the electrical conductivity that are expected will not be obtained at a temperature under 200°C or exceeding 700°C. Moreover, the reason for setting the aging temperature at 10 seconds – 10 hours is that the effects of aging treatment will not be seen if it is under 10 seconds, while if it exceeds 10 hours, there will be a marked reduction in strength due to over-aging. Furthermore, the cold draft is set at 10% or higher because if it is less than 10%, the improvement in strength and conductivity as a result of heat treatment during the next process will not be as good as expected.

When materials on which aging treatment and cold rolling have been performed as described above are heat treated for 10 seconds – 10 hours at a material temperature of 200 – 700°C, there is a marked increase in tensile strength as a result of this heat treatment. The strength and the electrical conductivity that are expected will not be obtained at a temperature less than 200°C or exceeding 700°C in this case. Moreover, the effects of heat treatment will not be seen when heat treatment time is less than 10 seconds, while it must not exceed 10 hours because there will be a marked drop in strength as a result of over-aging. Satisfactory results will usually be obtained with 20 seconds – 1 hour.

(Examples)

Examples will now be described.

Ingots with the various compositions relating to the present invention shown in Table 1 were melted and cast in a high-frequency melting furnace using electrolytic copper or oxygen-free copper as the starting material. These ingots were heated for 1 hour at 880°C and then hot-rolled into sheets with a thickness of 5 mm. After grinding the surfaces, they were heated for 30 minutes at 880°C and water-quenched. These solution-annealed materials were then aged for 1.5 hour at 450°C. They were further cold-rolled to sheets with a thickness of 0.5 mm. Heat treatment was then performed for 3 minutes at 450°C.

The strength of the samples prepared in this way was evaluated by determining the tensile strength, and the electrical conductivity was evaluated as conductivity (% IACS). Moreover, solderability was evaluated in 3 steps by the

perpendicular immersion method whereby [the sample] is immersed for 5 seconds in a solder bath (Sn 60% - Pb 40%) at $230 \pm 5^{\circ}\text{C}$ and then macroscopically checked for solder blisters. All of these results and the hot workability are shown in Table 1 together with the results for comparative alloys.

Furthermore, in Comparative Examples 16 and 17 in Table 1, the samples were solution-annealed, cold-rolled and aged.

By means of the production method for alloys relating to the present invention, alloys that are ideal for high-precision spring materials in that they have both strength and electrical conductivity rivaling those of beryllium copper alloys and they show good workability and solderability are produced, as is clear from Table 1.

Table 1.

	No.	Alloy composition (wt%)				Tensile strength (kg/mm ²)	Electrical conductivity (% IACS)	Solderability	Hot workability
		Cu	Ti	Sn	Auxiliary components				
Examples of this invention	1	Remainder	2.0	1.8	---	120	30	O	O
	2	"	1.6	2.3	---	115	32	O	O
	3	"	1.1	3.4	0.28 Ni, 0.08 Si	95	27	Δ	O
	4	"	1.8	2.0	0.10 In, 0.08 Te	115	29	O	O
	5	"	2.2	1.9	0.35 Zr, 0.05 P	117	28	O	O
	6	"	2.7	1.8	0.11 Zn, 0.14 Al	119	23	O	O
	7	"	3.2	1.6	0.18 Al, 0.07 P	120	21	O	O
	8	"	3.6	1.5	0.41 Mn	122	20	Δ	O
	9	"	4.0	1.3	0.22 Mg, 0.13 Al	122	18	O	O
	10	"	4.4	1.0	0.10 Fe, 0.08 Cr	125	17	Δ	Δ
	11	"	4.8	0.8	0.07 Pb	130	15	Δ	Δ
	12	"	1.3	0.8	0.06 P	101	20	O	O
	13	"	4.1	3.0	0.12 Zn	120	22	Δ	O

Comparative examples	14	Remainder	--	--	1.9 Be, 0.3 Co	140	25	Δ	x
	15	"	5.0	--		120	8	Δ	X
	16	"	1.0	1.8		72	22	O	O
	17	"	4.5	1.0		98	12	Δ	Δ

O: Good Δ: Average x: Poor

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審査請求 未請求 発明の数 2 (全3頁)

⑭ 発明の名称 高力高導電性銅基合金の製造方法

⑮ 特 願 昭60-270785

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1. 発明の名称

高力高導電性銅基合金の製造方法

2. 特許請求の範囲

(1) 0.1-5.0wt.%のTi, 0.1-5.0wt.%のSnを含有し、残部がCu及び不可避不純物からなる銅基合金を溶体化処理後、材料温度200~700℃で10秒~10時間の時効処理を行ない、続いて10%以上の冷間圧延を行なった後、さらに材料温度200~700℃で10秒~10時間の熱処理を施し、機械的強度及び導電性を向上させた高力高導電性銅基合金の製造方法。

(2) 0.1-5.0wt.%のTi, 0.1-5.0wt.%のSnを含有し、さらに0.005-1.0wt.%のP, 0.005-1.0wt.%のAl, 0.005-1.0wt.%のZn, 0.005-1.0wt.%のNi, 0.005-1.0wt.%のSi, 0.005-0.5wt.%のPb, 0.005-1.0wt.%のBe, 0.005-1.0wt.%のFe, 0.005-1.0wt.%のMn, 0.005-1.0wt.%のMg,

0.005-1.0wt.%のCr, 0.005-1.0wt.%のCo, 0.005-1.0wt.%のZr, 0.005-0.1wt.%のAs, 0.005-1.0wt.%のAg, 0.005-1.0wt.%のCd, 0.005-1.0wt.%のIn, 0.005-0.1wt.%のSb, 0.005-1.0wt.%のTe, 0.005-1.0wt.%のGe, 0.005-1.0wt.%のHfのうちから1種または2種以上を総量で0.005-2.0wt.%含有し、残部がCu及び不可避不純物からなる銅基合金を溶体化処理後、材料温度200~700℃で10秒~10時間の時効処理を行ない、続いて10%以上の冷間圧延を行なった後、さらに材料温度200~700℃で10秒~10時間の熱処理を施し、機械的強度及び導電性を向上させた高力高導電性銅基合金の製造方法。

3. 発明の詳細な説明

(目的)

本発明は、優れた機械的強度と良好な導電性を有する高力高導電性銅基合金の製造方法に関するものである。

(従来技術及び問題点)

高級精密ばね用材として現在使用されている高

力銅合金には、ベリリウム銅合金とチタン銅合金がある。ベリリウム銅合金は90-140kg/mm²という高い引張強さと20-25%IACSの良好な導電率を有するけれども、ベリリウムを約2%含有するため非常に高価となり、またベリリウムは劇毒性物質であることや、このベリリウム銅合金は250℃以上の温度で脆性が現れて合金の劣化をもたらすなどの欠点を有している。またチタン銅合金は、ばね性、耐熱性、耐摩耗性ではいずれもベリリウム銅合金に勝り、機械的強度もほぼ同程度でかつ安価であるという利点を有しているけれども、導電率が非常に劣るという大きな欠点を持っている。

このようなことからチタン銅合金の機械的強度を維持しつつ良好な導電性を得るために、このチタン銅合金にさらに第三元素としてSnを添加することが提案された。しかしながら、錫含有チタン銅合金を通常の溶体化処理後、時効処理、あるいは冷間加工と時効処理を施しても、引張強さはたかだか80-95kg/mm²に留まっており、ベリリウム銅合金の代替合金とするためにはさらに機械的

強度を向上させる必要があった。

(発明の構成)

本発明はかかる点に鑑みなされたもので、錫含有チタン銅合金の良好な導電率を維持しつつさらに機械的強度を向上させ、ベリリウム銅合金の有する経済性、毒性問題を回避した高級精密ばね用材として好適な諸条件を有する高力高導電性銅基合金の製造方法を提供するものである。

本発明は、0.1-5.0wt.%のTi、0.1-5.0wt.%のSnを含有し、残部がCr及び不可避不純物からなる銅基合金、及び0.1-5.0wt.%のTi、0.1-5.0wt.%のSnを含有し、さらに0.005-1.0wt.%のP、0.005-1.0wt.%のAl、0.005-1.0wt.%のZn、0.005-1.0wt.%のNi、0.005-1.0wt.%のSi、0.005-0.5wt.%のPb、0.005-1.0wt.%のBe、0.005-1.0wt.%のFe、0.005-1.0wt.%のMn、0.005-1.0wt.%のMg、0.005-1.0wt.%のCr、0.005-1.0wt.%のCo、0.005-1.0wt.%のZr、0.005-0.1wt.%のAs、0.005-1.0wt.%のAg、0.005-1.0wt.%のCd、0.005-1.0wt.%のIn、

ある。

Sn含有量を0.1-5.0wt.%とする理由は、0.1wt.%未満では期待する導電率が得られず、逆に5.0wt.%を超えると、熱処理を施しても固溶しきれない過剰のSnがTiと金属間化合物を生成、析出し、粗大析出粒子として合金の強度を著しく低下させるためである。

副成分として、前記所定量のP、Al、Zn、Ni、Si、Pb、Be、Fe、Mn、Mg、Cr、Co、Zr、As、Ag、Cd、In、Sb、Te、Ge、Hfからなる群より選択された1種または2種以上の総量を0.005-2.0wt.%とする理由は、0.005wt.%未満では副成分の添加によって期待される高い強度が得られず、また2.0wt.%を超えると導電率が著しく低下し、さらにはんだ付性及び熱間加工性が劣化するためである。

溶体化処理した材料を、材料温度200-700℃で10秒-10時間時効処理を行ない、引続き加工度10%以上の冷間圧延を加える。時効温度を200-700℃とする理由は、200℃未満あるいは700℃を超え

0.005-0.1wt.%のSb、0.005-1.0wt.%のTe、0.005-1.0wt.%のGe、0.005-1.0wt.%のHfのうちから1種または2種以上を総量で0.005-2.0wt.%含有し、残部がCu及び不可避不純物からなる銅基合金を溶体化処理後、材料温度200-700℃で10秒-10時間の時効処理を行ない、続いて10%以上の冷間圧延を行なった後、さらに材料温度200-700℃で10秒-10時間の熱処理を施し、機械的強度及び導電性を向上させた高力高導電性銅基合金の製造方法に関するものである。

(効果)

これにより、本発明の方法で製造すると、引張強さと導電率を同時に著しく向上させることができた。

(発明の具体的説明)

次に、本発明の合金成分と製造方法の限定理由を説明する。

Ti含有量を0.1-5.0wt.%とする理由は、0.1wt.%未満では期待する強度が得られず、逆に5.0wt.%を超えると導電率の向上が望めないため

る温度では期待される強度及び導電率が得られなく、また時効温度を10秒～10時間とする理由は、10秒未満では時効処理の効果が認められず、10時間を超えると過時効現象による強度の低下が著しいためである。さらに冷間加工度を10%以上としたのは、10%未満では次工程の熱処理による強度及び導電率の向上が期待するほど望めないためである。

上記のように時効処理及び冷間圧延した材料を、再び材料温度200～700℃で10秒～10時間熱処理すると、この熱処理によって材料の引張強さは著しく上昇する。この場合200℃未満あるいは700℃を超える温度では期待される強度及び導電率が得られない。また熱処理時間10秒未満では熱処理の効果が認められず、10時間を超えると過時効現象によって強度の低下が著しいため避けなければならない。通常30秒～1時間程度で十分な効果が得られる。

(実施例)

次に実施例について説明する。

法によって、ベリリウム銅合金にほぼ匹敵する強度と導電率を兼ね揃え、さらに良好な加工性とはんだ付性を示す高級精密ばね用材として好適な合金となる。

以下 余 白

第1表に示される本発明に係る各種成分組成のインゴットを、電気銅あるいは無酸素銅を原料として高周波溶解炉で溶解、鋳造した。このインゴットを880℃で1時間加熱し、引続き熱間圧延して厚さ5mmの板とした。而後880℃で30分間加熱し、水焼入れした溶体化処理材料に450℃で1.5時間の時効処理を施した。さらに冷間圧延で厚さ0.5mmの板とし、450℃で3分間の熱処理を加えた。

このようにして調整された試料の評価として、強度は引張試験、電気伝導度を導電率(%IACS)によって評価した。また、はんだ付性を垂直式浸漬法で230±5℃のはんだ浴(Sn60%-Pb40%)に5秒間浸漬してはんだのぬれの状態を目視観察することにより3段階で評価した。これらすべての結果と熱間加工性を比較合金とともに第1表に示した。

なお第1表において比較例16、17は溶体化処理後、冷間圧延を行い、その後時に時効処理した材料である。

第1表に示すごとく本発明に係る合金の製造方

第1表

番号	合金組成 (wt.%)				引張強さ kg/mm ²	導電率 %IACS	はんだ 付性	熱間 加工性
	Cu	Ti	Sn	副成分				
1	残	2.0	1.8	---	120	30	○	○
2	"	1.6	2.3	---	115	32	○	○
3	"	1.1	3.4	0.28 Ni 0.08 Si	95	27	△	○
4	"	1.8	2.0	0.10 In 0.08 Te	115	29	○	○
5	"	2.2	1.9	0.35 Zr 0.05 P	117	28	○	○
6	"	2.7	1.8	0.11 Zn 0.14 Al	119	23	○	○
7	"	3.2	1.6	0.18 Al 0.07 P	120	21	○	○
8	"	3.6	1.5	0.41 Mn	122	20	△	○
9	"	4.0	1.3	0.22 Mg 0.13 Al	122	18	○	○
10	"	4.4	1.0	0.10 Fe 0.08 Cr	125	17	△	△
11	"	4.8	0.8	0.07 Pb	130	15	△	△
12	"	1.3	0.8	0.06 P	101	20	○	○
13	"	4.1	3.0	0.12 Zn	120	22	△	○
14	"	—	—	1.9 Be 0.3 Co	140	25	△	×
15	"	5.0	—		120	8	△	×
16	"	1.0	1.8		72	22	○	○
17	"	4.5	1.0		98	12	△	△

○:良 △:普通 ×:悪